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Living Alternating Ring-Opening Metathesis Polymerization Based on Single Monomer Additions

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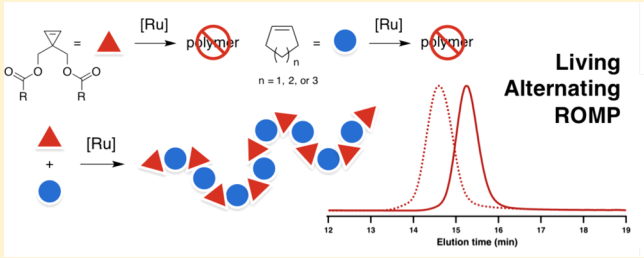
Supporting Information

ABSTRACT: By judiciously modulating the ring strain and sterics, we developed a class of disubstituted cyclopropenes that selectively underwent single monomer addition in ring-opening metathesis but readily underwent alternating ring-opening metathesis polymerization with low-strain cyclic olefins in a living fashion. The substituents on cyclopropenes effectively inhibited homoaddition and prevented secondary metathesis on the polymer backbone. The resulting polymers had controllable molecular weights and end groups, very low dispersities, and high regularity in microstructure under optimized conditions. ^{1}H and ^{13}C NMR spectroscopy and MALDI-TOF MS showed a rigorously alternating sequence. Interestingly, disubstituted cyclopropenes were found to present zero-order kinetics, indicating their rapid single addition and the rate-determining ring opening of the low-strain olefin.



INTRODUCTION

Controlling the microstructure and monomer sequence of synthetic polymers is a central challenge in polymer chemistry.[1−3] Polymers with controlled microstructures and sequence may give rise to higher order structures as well as properties that are unobtainable from polymers lacking these regulations. Without using solid supports, a homogeneous polymerization capable of controlling microstructure and sequence is highly desired to obtain large quantities of materials and to avoid iterative protection−deprotection cycles. We reasoned that, in order to synthesize sequence-defined polymers by sequential monomer additions under homogeneous conditions, one needs a system that (1) is a living polymerization, (2) allows for iterative single monomer additions rather than a Poisson distribution, and (3) does not permit chain transfer or other side reactions to scramble the sequence.

In pursuit of this goal, one might look to adapt alternating polymerization systems, where the copolymerization of two types of monomers A and B results in repeating AB dyads. Radical polymerization of styrene and maleic anhydride is one of the best known alternating systems. In recent years, Lutz and co-workers have harnessed these monomers' propensity for alternation to synthesize polystyrenes with narrow segments of *N*-substituted maleimides at desired positions by time-regulated additions of these maleimides.[4−6] A similar strategy has been used with norbornenes.[7] However, these monomers are often positioned within a narrow segment but not exclusively controlled, and controlling stereochemistry remains challenging. Transition metal catalysts can be tuned to differentiate the sterics and/or electronics of the incoming monomers at the propagating site to result in alternating polymerization and controlled tacticity.[8−14] Different catalyst or monomer designs have been used to achieve alternating ring-opening metathesis polymerization (AROMP).[14−28] However, alternating polymerizations normally rely on the competition between homopropagation versus cross-propagation, and one or both of the monomers can still be homopolymerized. Kinetic control based on the rate competition can lead to statistical instead of exclusive control of alternating dyads with statistical errors of small homoaddition segments.

Monomers that undergo single additions are particularly interesting but extremely rare. Sampson and co-workers developed an interesting AROMP system based on 1-carboxylate-cyclobutene, which reacts with a ruthenium alkylidene only once to form an enoic ruthenium carbene without homopropagation. This monomer was shown to undergo AROMP with cyclohexene.[23−27] However, this system led to high molar-mass dispersity ($Đ_M$), limited molecular weight (MW), and formation of macrocyclic species, due to extensive chain transfer occurring during polymerization. Very recently, the same group reported an interesting class of isomerized bicyclic carboxamides that led to high MW AROMP polymers.[28]

We considered cyclopropene (CP) as a privileged monomer family that can be potentially tuned to satisfy all the aforementioned challenging requirements for homogeneous sequence-defined polymerization. Highly strained CP provides a large thermodynamic driving force for ring opening, and various substitutions on CP are readily accessible to adjust the sterics proximal to the olefins in both the monomer and in the

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resulting polymer. Therefore, judiciously designed CP derivatives may suppress reactivity toward homopropagation but remain highly reactive toward ring opening to achieve rapid single CP addition. Furthermore, the substituents remain proximal to the polymer backbone olefin to hinder secondary metathesis (both intermolecular chain transfer and intramolecular "backbiting"). Surprisingly, despite being the most strained cyclic olefins, CP derivatives have rarely been investigated for ROMP. Only simple 3,3-dimethyl, 3-methoxyethyl-3-methyl, and 3-methyl-3-phenyl CPs have been reported to undergo homopolymerization via ROMP.[29−32]

Herein we report the first example of AROMP that possesses all the characteristics of a living polymerization: controlled MW and end groups, very low dispersities, and precisely alternating sequences. This system is built on a class of 1,1-disubstituted CPs we discovered that undergoes selective single ring-opening metathesis without homopolymerization but readily undergoes AROMP with a series of low-strain cyclic olefins (LSCOs) in a living fashion. The alternating polymers are highly regular and devoid of stereocenters upon hydrogenation. Interestingly, all the CPs we studied exhibited zero-order kinetics in AROMP, indicating that the ring opening of CPs is fast and not rate-determining in the alternating copolymerization.

RESULTS AND DISCUSSION

Single Monomer Addition. Usually disubstitution is required for CPs to be stable at ambient conditions. We focused on the bench-stable, symmetrical 1,1-disubstitued CPs **2** and **3** to investigate their reactivity toward ring-opening metathesis. We hypothesized that the steric bulk introduced from both faces of the olefin would inhibit their tendency toward homopolymerization. To investigate the reactivity, 1 equiv of Grubbs catalyst [$(H_2IMes)(pyr)_2Cl_2RuCHPh$] **1** was added to 10 equiv of **2** and **3**, and the reaction was monitored by ^1H NMR spectroscopy. CP **2** was very slow to react with **1**, with only ∼30% of the catalyst initiating and generating the ring-opened product after 7 h. Interestingly, with reduced sterics at the olefin, CP **3** rapidly reacted with 10 mol % **1** to form the ring-opened product with a concurrent depletion of the benzylidene signal on the original catalyst **1**, indicating complete initiation. Excitingly, CP **3** conversion plateaued at exactly 10 mol % in 15 min, corresponding to the ring opening of only 1 equiv of monomer (Figure 1). After 12 h, no homopolymerization of **3** was observed. We propose that the homopolymerization of **3** is inhibited because the steric environment on the active Ru complex is too hindered for another equivalent of **3** to react. As such, **3** represents a unique class of monomers capable of selective single addition while possessing a high thermodynamic driving force for ring opening.

Alternating Polymerization with Low-Strain Cyclic Olefins. LSCOs have little or no thermodynamic driving force for polymerization, with the small enthalpic gain upon ring opening often being offset by a loss of entropy upon polymerization. Therefore, a critical concentration exists for LSCOs below which no polymer is formed.[33−36] Below the critical concentration, LSCOs reach an equilibrium between opened and closed forms. Following the addition of one CP, unhindered LSCOs could react with the hindered metal carbene to relieve the steric hindrance and allow rapid addition of another CP, leading to an alternating sequence.

We investigated cyclopentene (CPen), cyclohexene (CHex), and cycloheptene (CHep) as examples of LSCOs to probe the

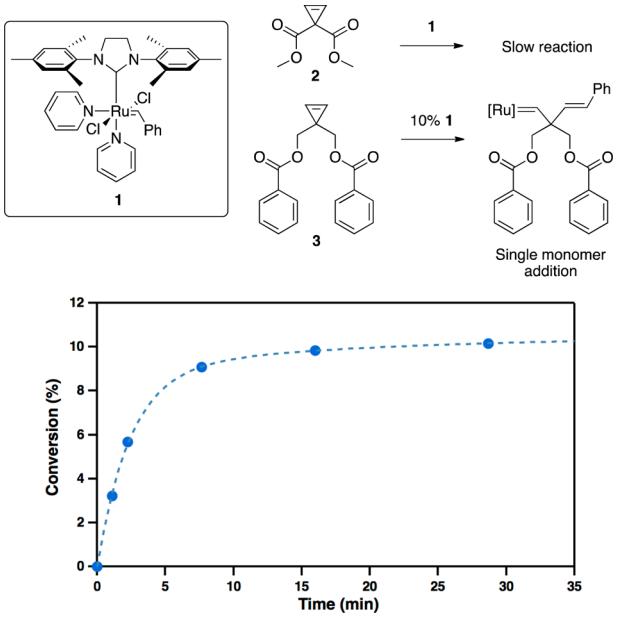

Figure 1. Conversion of **3** vs time showing selective single addition of **3** to **1**. Conditions: $[\mathbf{3}]_0$ = 0.1 M in $CDCl_3$ at 22 °C; $[\mathbf{3}/\mathbf{1}]_0$ = 10:1.

efficiency and fidelity of their AROMP with CPs. Although neither **3** nor these LSCOs alone formed any detectable polymer at 0.1 M, which was the concentration used for their copolymerizations, mixtures of **3** and all the LSCOs formed high MW polymers.

Interestingly, copolymers resulting from the CP/CHex pair had very low dispersities (<1.1) while copolymers from CP/CPen and CP/CHep had significantly larger dispersities, typically around 1.3−1.4, although all the resulting polymers had monomodal molecular weight distributions (MWDs) (Figure 2). Varying the ratio of CP to **1** resulted in polymers with precisely controlled MWs and dispersities <1.1 (Table 1, entries 5−7; Figure S1), indicative of a well-controlled living

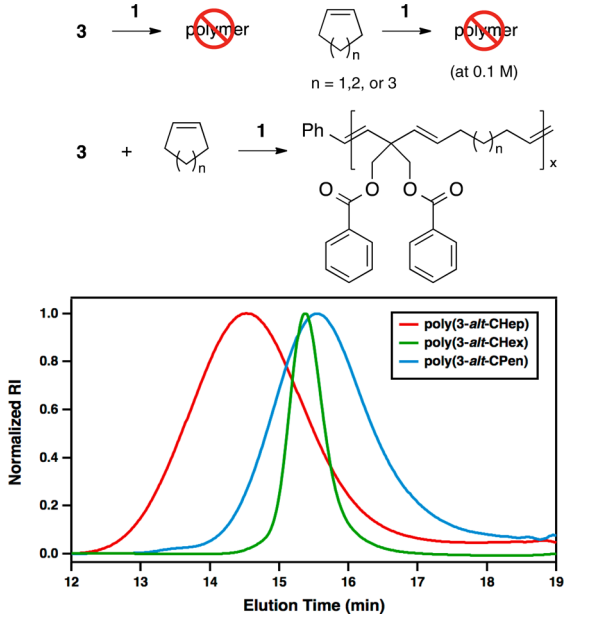

Figure 2. GPC traces of polymers produced from AROMP of **3** and CPen, CHex, or CHep (Table 1 entry 1, 3, and 5, respectively).

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Table 1. AROMP of 1,1-Disubstituted Cyclopropenes and Low-Strain Cyclic Olefins

entry	CP	LSCO	$[CP/1]_0$	$[LSCO/CP]_0$	$[CP]_0$[a] (M)	time (h)	$M_{n,\,theo}$[b] (kDa)	$M_{n,\,MALLS}$[c] (kDa)	$Đ_M$[c]	conv.[d]
1	**3**	CPen	50	1	0.1	5.5	15.2	12.2	1.30	81%
2	**3**	CPen	50	1	0.01	22	15.0	12.1	1.16	80%
3	**3**	CHep	50	1	0.1	5.5	18.2	14.6	1.34	90%
4	**3**	CHep	50	1	0.01	22	18.4	14.1	1.09	91%
5	**3**	CHex	50	20	0.1	3	17.9	18.3	1.04	92%
6	**3**	CHex	100	20	0.1	6	34.0	38.7	1.03	83%
7	**3**	CHex	200	20	0.1	17	78.7	94.0	1.08	96%
8	**4a**	CHex	50	20	0.1	6	20.9	22.0	1.05	98%
9	**4b**	CHex	50	20	0.1	7	21.1	25.2	1.05	92%
10	**4c**	CHex	50	20	0.1	4	21.6	27.8	1.03	96%
11	**4d**	CHex	50	20	0.1	4.5	28.6	25.6	1.02	97%
12	**5**	CHex	50	20	0.3	72	8.5	8.1	1.07	64%

[a]Initial CP concentration. [b]Theoretical MW. [c]Determined by GPC MALLS analysis in THF. [d]CP conversion determined by ^{1}H NMR analysis of polymerization.

polymerization. ^{1}H and ^{13}C NMR analyses unambiguously revealed the perfectly alternating structure of poly(3-*alt*-CHex). The ^{1}H NMR spectrum contained sharp resonances for the backbone olefinic protons, being a doublet and a doublet of triplets, corresponding to only the alternating dyads (Figure 3a). ^{1}H−^{1}H COSY clearly showed strong cross peaks corresponding to the alternating dyads (Figure 3b). The sharp ^{1}H NMR peaks indicate regular microstructures. We could easily determine the coupling constant between the two olefinic protons to be $^3J_{HH}$ = 16.0 Hz. This large coupling constant is characteristic of a *trans* olefin configuration, which was also revealed by a relatively intense peak at 976 cm^{-1} in the IR spectrum (Figure S3). A small population of *cis* olefin was present, which overlapped with the *trans* proton peaks. Only two olefinic peaks were observed from the sharp and relatively simple ^{13}C NMR resonances (Figure 3c), again indicating the alternating sequence of the polymer. At last, MALDI-TOF mass spectrometry provided further evidence for an exclusively alternating sequence. Two sets of peaks were observed, with the more intense set **A** corresponding to the alternating polymer with a terminal ring-opened CHex and the smaller set **B** corresponding to a terminal ring-opened **3** (Figure 4). Essentially, only masses of the integral numbers of the alternating dyad plus one terminal repeat unit were observed (an additional set of very low intensity unidentified peaks below 4000 Da could be seen, but the masses do not correspond to any species with homoadditions of either monomers). Furthermore, the masses also revealed the expected end groups, benzylidene on one end and methylene on the other end resulting from the initiator and the vinyl ether quenching reagent, respectively. Overall, these results are indicative of a well-controlled living alternating polymerization.

The fact that very low dispersities were obtained in the CP/CHex pair indicated that the formed backbone olefins in alternating dyads are sufficiently hindered and do not undergo secondary metathesis. To further confirm the absence of chain transfer, isolated poly(3-*alt*-CHex) was added with a Grubbs II catalyst and excess *cis*-3-hexene, an effective chain transfer agent (CTA) in ROMP. No change to the GPC trace of the polymer was observed (Figure S4). Were the backbone olefins susceptible to chain transfer, the addition of CTA should have decreased the observed MW. Therefore, it is clear that chain transfer suffered by other AROMP systems is prevented via appropriately designed CPs.

The backbone olefins in the alternating dyads between CP and CPen, CHex, or CHep should all be shielded by the same sterics on the CP units against chain transfer. However, ^{1}H NMR spectra of the copolymers from CPen and CHep indicated a small amount of homoaddition from CPen and CHep (Figures S5 and S7), which resulted in unhindered olefins that are susceptible to chain transfer. This was confirmed by the same *cis*-3-hexene chain transfer test, which yielded lower MW polymers within 1 h for both poly(3-*alt*-CPen) and poly(3-*alt*-CHep) (Figure S4). The homoaddition of CPen and CHep can be explained by the small yet negative $\Delta G°$ for their ROMP, −0.6 and −1.6 kcal/mol at 25 °C, respectively.[37] Occasional homoaddition occurred at 0.1 M, even though neither CPen nor CHep formed any polymeric species at this concentration. We significantly suppressed homoaddition of CPen and CHep by carrying out their AROMP at [CP] = [CPen or CHep] = 0.01 M, well below their critical concentrations. Satisfyingly, narrowly dispersed poly(3-*alt*-CPen) and poly(3-*alt*-CHep) were obtained with much lower dispersities (Table 1, entries 2 and 4). Furthermore, no homoaddition resonances were observed in the ^{1}H NMR spectra under these conditions (Figures S8−S9).

An excess of CHex ([CHex:CP] of 20:1) was used for the AROMP of CHex due to the otherwise significantly longer polymerization times (>24 h) in comparison to CPen and CHep. In the presence of an excess of CHex, if the reaction was prolonged after complete CP conversion, we observed that the resulting polymer began to develop a high MW shoulder. Estimation of the shoulder peak indicated that the MW was approximately double of the main peak, which suggested that the high MW species may have formed from selective chain-end coupling after full conversion. We hypothesized that the chain coupling resulted from cross metathesis between unhindered ring-opened CHex olefins at the chain ends after the depletion of CP (Figure S10). The middle olefin formed due to chain coupling will then be the only unhindered olefin in the resulting polymer, so it should be cleaved by cross metathesis with *cis*-3-hexene. In fact, with the addition of *cis*-3-hexene, the high MW shoulder was removed to recover the narrowly dispersed peak and restore the perfectly alternating sequence (Figure S10).

Polymerization Kinetics. A range of dibenzoyl CP derivatives **4a**−**d** with varying functionalities and electronics can be copolymerized with CHex to yield perfectly alternating copolymers in high MWs, low dispersities, and high monomer conversions (Figure 5). 1,1-Disubstituted CP **5** with aliphatic

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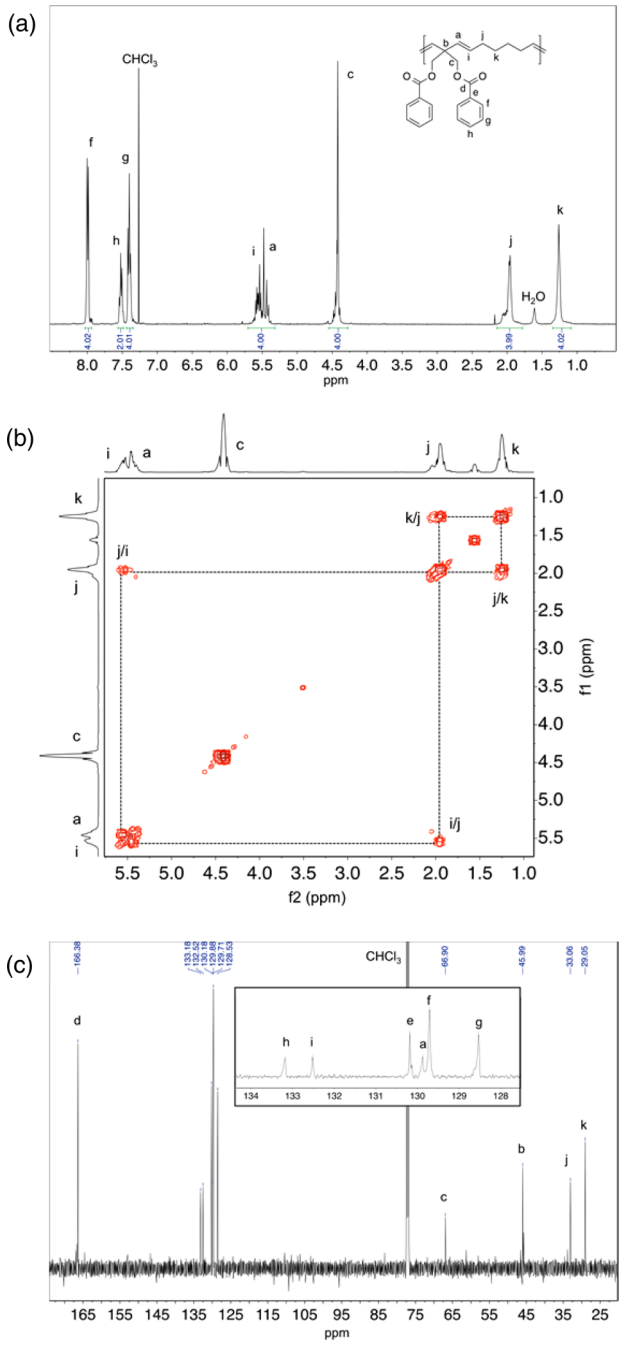

Figure 3. (a) ^{1}H NMR, (b) ^{1}H−^{1}H COSY, and (c) ^{13}C NMR spectra of poly(3-*alt*-CHex).

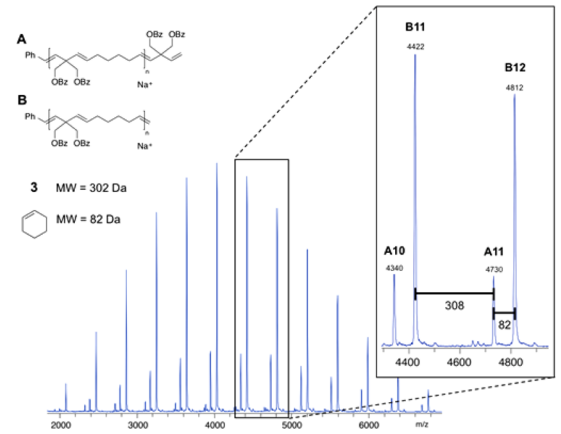

Figure 4. MALDI-TOF MS spectrum of poly(3-*alt*-CHex).

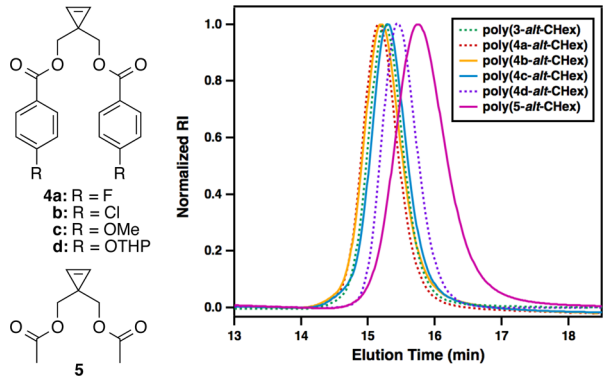

Figure 5. GPC traces of various CP/CHex AROMP polymers.

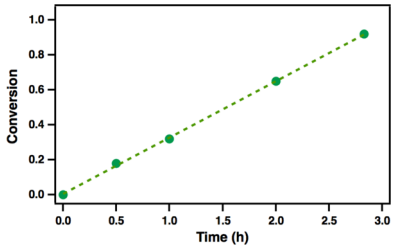

Figure 6. Zero-order kinetics for CP observed in CP/CHex AROMP. Conditions: $[3]_0$ = 0.1 M; [CHex:**3**] = 20; conversion of CP determined by ^{1}H NMR spectroscopy.

ester substituents also resulted in living AROMP, although considerably slower than dibenzoyl CPs. We suspect that the slower yet still living AROMP for CPs with more electron-rich aliphatic ester substituents may be due to weak coordination of ester to the propagating catalyst. The detailed influence of electronics in the reactivity of disubstituted CPs is a subject of future study.

Interestingly, kinetic measurements of CP/CHex AROMP revealed that the rate of polymerization to be first order in CHex and the catalyst (Figure S11), but surprisingly zero-order up to very high conversions in all the CP derivatives **4a**−**d** and **5** we have studied (Figures 6 and S12). These results imply that the addition of CPs is always fast and never the rate-determining step, even in the presence of a large excess of CHex, while the addition of CHex is slow and rate-determining. This polymerization rate law has profound implications in future developments of homogeneous sequence-controlled polymerizations.

CONCLUSION

We have developed a living AROMP system based on various 1,1-disubstituted CPs and LSCOs. Significantly, these hindered CPs undergo single monomer addition. The ability for selective single monomer addition resulted in precisely controlled alternating sequences. The sterics proximal to backbone olefins prevented chain transfer. Therefore, perfectly alternating copolymers were obtained in high MWs, low dispersities, and high monomer conversions. Kinetic measurements indicated that the addition of CPs was considerably fast and the addition of CHex was the rate-determining step for this AROMP system. We will continue to explore the olefin metathesis

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reactivities of diverse CPs and apply the single monomer addition strategy to control the primary sequence of synthetic polymers.

EXPERIMENTAL SECTION

Materials. **1** was prepared following the literature procedure.[38] Compounds **2**, **3**, and **5** were synthesized following the literature procedure.[39] Cyclohexene was obtained from Sigma-Aldrich and distilled before use. All other materials were obtained from commercial sources and used as received.

Characterizations. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ using 400, 500, or 600 MHz Varian NMR spectrometers. Chemical shifts are reported in ppm relative to $CDCl_3$ (δ = 7.27). MALDI-TOF mass spectrometry was performed on a Bruker Microflex LRF at the Stanford University Mass Spectrometry Facility. GPC was performed in THF on two PLgel 10 μm mixed-B LS columns (Agilent Technologies) connected in series with a DAWN 8+ multiangle laser light scattering (MALLS) detector and an Optilab T-rEX differential refractometer (both from Wyatt Technology). No calibration standards were used, and dn/dc values were obtained by assuming 100% mass elution from the columns.

General Procedure for Living AROMP. The desired amounts of CP and LSCO monomers were added in vials equipped with a stir bar under a N_2 atmosphere. Dry, degassed THF was then added to the vials. A stock solution of **1** was prepared in THF (the bromopyridine Grubbs III catalyst gave qualitatively similar polymerization results), and the required amount of **1** was quickly injected to each vial to begin polymerization at room temperature. CP conversion was periodically determined by ^{1}H NMR spectroscopy. Upon completion of the polymerization, the reactions were terminated by the addition of a few drops of ethyl vinyl ether. The resulting polymers were isolated by precipitating into MeOH and drying under vacuum.

General Procedure for Secondary Metathesis Studies. Polymers were dissolved in dry, degassed THF under a N_2 atmosphere. The desired amounts of the Grubbs II catalyst and *cis*-3-hexene were added from their stock solutions in THF. Reactions were stirred at room temperature. Aliquots were taken at desired times for GPC analysis to assess the presence of any secondary metathesis (chain transfer) on the polymers being examined.

ASSOCIATED CONTENT

Supporting Information

Additional synthetic procedures, NMR spectra, GPC traces, and experimental procedures are available in the Supporting Information. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b05497.

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Notes

The authors declare no competing financial interest.

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